# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

## Phthalocyanine Sulfonhydrazides

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 230, Park Avenue, New York, County and State of New York, United States of America (Assignees of ARTHUR LAWRENCE FOX, a citizen of the United States of America, of 118, Parker Avenue, Easton, County of Northampton, Commonwealth of Pennsylvania, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new phthalocyanine derivatives.

The term phthalocyanine is used herein in the generic sense to define tetraazaporphins in which each of the four pyrrole nuclei is fused to an aromatic nucleus, e.g., phenyl, diphenyl, naphthyl, anthranyl, etc., of which phthalocyanine itself (tetrabenzotetraazaporphin) is a well-known example. The phthalocyanine molecule may be metal free or contain a metal in complex combination, for example, copper, cobalt, nickel, iron and aluminium.

The invention concerns new compounds which are phthalocyanine sulfonhydrazides and the preparation thereof which may be accomplished by condensing a phthalocyanine sulfonylchloride with a hydrazine which may be hydrazine itself or a primary or secondary alkyl, substituted alkyl, alicyclic, aryl or heterocyclic hydrazine. All of these hydrazines contain a reactive hydrogen atom attached to one of the nitrogens of the —N.N— group.

The preparation of the new phthalocyanine derivatives can be effected by reacting the corresponding phthalocyanine sulfonylchloride with the hydrazine at room or elevated temperatures in the presence of a suitable reaction diluent, for example, water, alcohol, acetone, nitrobenzene or an excess of the hydrazine.

In addition to hydrazine itself, suitable hydrazines for the preparation of the new compounds are, for example, methyl, ethyl, propyl and butyl hydrazine, sym. and asym. dimethyl hydrazine, N,N - bis(β - hydroxyethyl) hydrazine, cyclohexyl hydrazine, benzyl hydrazine, phenyl hydrazine, *p*-chlorophenyl hydrazine, *p* - bromophenyl hydrazine, *p*-sulfophenyl hydrazine, *o*-, *m*-, or *p*-tolyl hydrazine, *p*-xylyl hydrazine, 3-hydrazinoaniline, sym. and asym. diphenyl hydrazine, triphenyl hydrazine, naphthyl hydrazine, α-methylphenyl hydrazine, α - ethyl - phenyl hydrazine, α,β - dimethyl - phenyl hydrazine, 2 - hydrazinopyridine, α-quinozyl hydrazine, α-lepidyl hydrazine, α-hydrazoquinoline, 4-aminomorpholine, 3 - hydrazino - 1,2,4 - triazole and 5-hydrazinotetrazole.

The new products are phthalocyanines containing attached to the arylene nuclei one or more unsubstituted or alkyl, substituted alkyl, alicyclic, aryl or heterocyclic sulphonhydrazide groups. In addition to the sulfonhydrazide group or groups, other substituents, such as halogen atoms, e.g., chlorine, or amino or carboxy radicals may be attached to the arylene nuclei of the phthalocyanines. The number of the sulfonhydrazide groups on the arylene nuclei may be varied depending on the number of sulfonylchloride groups on the arylene nuclei of the corresponding phthalocyanine sulfonylchlorides. In some instances the new products may also contain attached to the arylene nuclei one or more sulfonic acid groups, either free or as the hydrazine salt, not all of the sulfonylchloride groups being converted to sulfonhydrazide groups in the reaction. They range in color from bluish-green to green, being somewhat greener in shade than the phthalo-

cyanine sulfonamides described in Specification No. 520,199. They may be employed as pigments or as dyestuffs depending on their solubility characteristics.

Dyestuffs which are soluble in dilute aqueous caustic alkali, e.g., sodium, potassium or lithium hydroxide, may be prepared by introducing onto the arylene nuclei of the phthalocyanine molecule a plurality of sulfonhydrazide groups containing a free hydrogen atom on the nitrogen of the sulfamyl portion thereof. Compounds of this character are capable of dyeing directly cotton, wool, and silk, showing particularly good affinity for silk. Employed in the form of their soluble alkaline salts, particularly sodium, potassium, ammonium or lithium, they are suitable as colorants for the preparation of writing ink fluids, showing to particular advantage in writing inks rendered quick drying by small amounts of caustic alkali, being, generally, quite stable in dilute aqueous caustic alkali.

The starting phthalocyanine sulfonylchlorides employed in the preparation of the phthalocyanine sulfonhydrazides may be obtained by reacting chlorosulfonic acid with the corresponding phthalocyanines at an elevated temperature as described in Specification No. 515,637. They may also be made from the corresponding phthalocyanine sulfonic acids or their salts by treatment with phosphorus pentachloride.

The invention is further illustrated by the following specific examples to which, however it is not to be limited. Parts are by weight unless otherwise noted.

EXAMPLE 1.

Ten parts of hydrazine hydrate is dissolved in 50 parts of water and 10 parts of copper phthalocyanine tetrasulfonylchloride added. Stirring is then instituted and continued for several hours at room temperature until dissolution is complete. The reaction mixture is then stirred into 4 volumes of 10% hydrochloric acid and the precipitated dyestuff filtered and dried. There is obtained a bluish-green powder which is quite soluble in dilute aqueous sodium hydroxide. The yield is 89.3%.

EXAMPLE 2.

Twenty parts of copper phthalocyanine tetrasulfonylchloride is stirred into an excess of phenyl hydrazine which is heated on the steam bath. The mixture at once begins to foam and the reaction takes place quite rapidly. In 30—45 minutes only a dark green solid material remains. This material is then stirred into approximately 4 volumes of 10% hydrochloric acid and the precipitate filtered and dried. The product thus obtained is somewhat soluble in dilute aqueous sodium hydroxide and dyes silk a vivid green shade. The yield is 90.4%.

EXAMPLE 3.

Twenty parts of copper phthalocyanine tetrasulfonylchloride is stirred into a mixture of 30 parts of 4-sulfophenylhydrazine in 100 parts of nitrobenzene. The resulting mixture is heated to 50—60° C. while stirring and then allowed to slowly cool to room temperature after which stirring is continued for several hours. The nitrobenzene is then removed by means of steam distillation and the resulting aqueous suspension acidified with 10% hydrochloric acid. The precipitated product is filtered and dried. A green powder is obtained which is quite soluble in dilute aqueous sodium hydroxide and is quite satisfactory for use as a dyestuff for writing ink fluids. The yield is 72%.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of preparing a phthalocyanine sulfonhydrazide which comprises condensing a phthalocyanine sulfonylchloride with a hydrazine.

2. The process as defined in claim 1, wherein the hydrazine is unsubstituted hydrazine.

3. The process as defined in claim 1, wherein the hydrazine is an alkyl hydrazine.

4. The process as defined in claim 1, wherein the hydrazine is an alicyclic hydrazine.

5. The process as defined in claim 1, wherein the hydrazine is an aryl hydrazine.

6. The process as defined in claim 1, wherein the hydrazine is a phenyl hydrazine.

7. Phthalocyanine sulphonhydrazides whenever prepared by a process of any of the preceding claims or by a process which is the obvious chemical equivalent thereof.

Dated this 2nd day of July, 1946.

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